

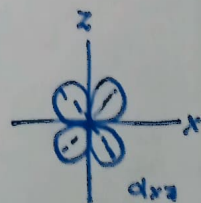
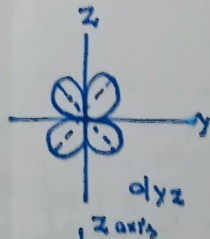
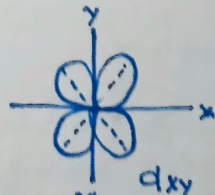
Limitations of Valence Bond theory

Pauling's Valence bond theory explains the chemistry of Co-ordination Complexes satisfactorily but failed to explain some of the aspects.

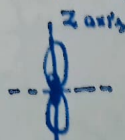
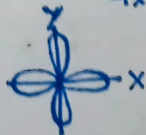
- (i) The Particular behavior of divalent Nickel, Palladium, Platinum and trivalent Gold, i.e. V.B.T does not explain the behaviour of Complex having d^8 Central ion (Ni^{2+} , Pd^{2+} , Au^{3+} ... etc) by forming the expected sp^3 Co-ordinated Complex.
- (ii) It is also not clear why this theory prefers only Square Planar Geometry of Complex to other possible Geometry such as tetrahedral and trigonal bipyramidal with Co-ordination No. 5.
- (iii) Pauling's theory is unable to explain why Square Planar Complexes Cu^{2+} ions like $[Cu(NH_3)_4]^{2+}$ are not reducing agent like inner-orbital octahedral Complexes of Co^{2+} (d^7 system). Although in both the cases promotion of a non bonding d -electron to some higher energy level (s - s level) is required.
- (iv) Pauling's idea offered a little or no explanation to absorption spectra of Complexes.
- (v) It does not explained why certain Complexes are more labile (changeable) than the others.
Labile Complexes are those in which one ligand can be easily displaced by the other ligand. On the other hand inert Complexes are those in which displacement of ligand is very slow.
- (vi) It does not take into consideration about the splitting of d -energy levels.
- (vii) It does not account for the relative energies of different structures.

Before considering the Crystal field theory. It's essential to know about the shape of d -orbitals are first, they are shown below:

(i) d_{xy} or t_{2g} set
(d_{xy} , d_{yz} , d_{zx})
(Between the axis)



(ii) $d_{x^2-y^2}$ or e_g set
($d_{x^2-y^2}$, d_{z^2})
(Along the axis)



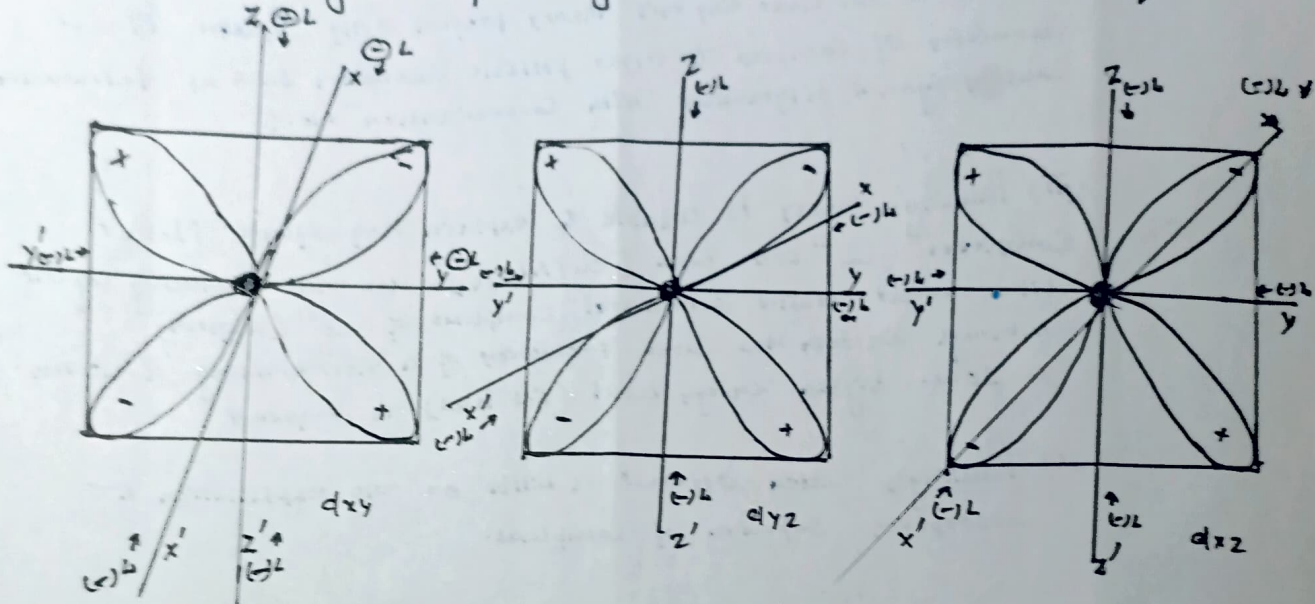
In 1st set d_{xy} or t_{2g} there is 3 orbitals designated as d_{xy} , d_{yz} & d_{zx} and they have Max. Probability region between x , y and z axes. The 2nd set $d_{x^2-y^2}$ or e_g consist of two $d_{x^2-y^2}$ & d_{z^2} orbital. $d_{x^2-y^2}$ is oriented in xy plane and it has Max. Probability region along x and y axis. But d_{z^2} orbital is oriented along z axis and its Max. Probability region is along z axis.

C.F. Splitting of d-orbitals:

The energy difference between d_{xy} (d_{xy}, d_{yz}, d_{zx}) and d_{z^2} or $d_{x^2-y^2}$ ($d_{x^2-y^2}, d_{z^2}$) level is represented by Δ and it is termed as Crystal field Splitting.

The Crystal field splitting energy Δ is frequently measured in terms of a parameter Dq .

The magnitude of splitting is conventionally set at $10Dq$.



In C.F. Splitting of d-orbitals, the d-orbitals are lying in the direction of the approaching ligands, C.F.T regards the anionic ligands as negative point charge & Neutral ligands as dipole.

